similarly, this indicates strongly that the global rotational diffusion dominates our system (ϕ_{global}; Figure 7). That is, the average PRODAN-$(N_2O)_x$ cluster apparently moves as a unit;[91] there is minimal contribution from the PRODAN motion independent of the cluster.

We are currently investigating alternative fluorescent probes for characterization of supercritical CO_2. PRODAN is unacceptable because of its long fluorescence lifetime ($\approx$2 ns) in the interesting region near the critical point. In these experiments, it is imperative that the fluorescence lifetime of the solute probe be on the same time scale as the expected rotational diffusion (tens of picoseconds). If the lifetime is too long, the observed anisotropy will provide no information about rotational diffusion (see eq 2). Thus, we are investigating several short-lived fluorescent probes which emit in the visible, and whose fluorescence lifetime is relatively insensitive to the local environment.

Acknowledgment. Financial support was provided by the U.S. Department of Energy (DE-FGO2-90ER14143) and an Allied Signal Fellowship (T.A.B.). We also acknowledge Bill Fain of SLM Instruments for the calibration lamp.

Registry No. N_2O, 10024-97-2; PRODAN, 70504-01-7.

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[91] One should not loose site of the dynamical nature of these clusters.[18] Clearly, there is exchange of fluid species on a picosecond time scale; thus, we can at best only speak about average cluster properties.

The First Direct Observation of Magnetic Field Effects on the Dynamic Behavior of Radical Pairs Involving Group 14 Silicon and Germanium Centered Radicals

Masanobu Wakasa, Yoshio Sakaguchi, and Hisaharu Hayashi*

Contribution from the Molecular Photochemistry Laboratory, The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan. *Received April 27, 1992*

Abstract: Laser flash photolysis was performed on micellar solutions and oil emulsions of organosilicon and organogermanium compounds ($(\text{aryl})_n\text{Me}_{4-n}\text{E}$: E = Si or Ge) in the absence and presence of magnetic fields at room temperature. The dynamic behavior of the silyl and germyl radicals formed upon decomposition of the triplet states was directly observed. The lifetime of the radical pair of group 14 element centered and aryl radicals and the yields of the escaped silyl and germyl radicals were observed to increase with magnetic field strength increasing from 0 to 1.35 T.

Magnetic field effects on the chemical reactions of radical pairs and biradicals have received considerable attention.[1-3] Although extensive studies on the effects have been made previously, there have been only a limited number of studies on the reactions of radicals involving heavy atoms such as Si, S, Ge, and Sn. Recently, we carried out a laser flash photolysis study of phenacyl phenyl sulfone in a micellar solution at room temperature and found magnetic field effects on the yield of the escaped benzenesulfonyl radical.[4] In the reactions involving germyl and ketyl radicals, we also found magnetic field effects on the yield of the ketyl radical.[5] The observed magnetic field effects in these reports, however, were much smaller than those reported in the reactions of ketones in micellar solutions where carbon (C)-centered radicals were produced.[6] It is believed that the deficiencies in the effects are due to the spin-orbit (SO) interaction of heavy atoms such as Si and Ge.[1-3]

The key problem in establishing the importance of magnetic field effects on the reactions involving such heavy atoms is to find a suitable reaction system in which the influence of the SO interaction can be suppressed. Currently, the photochemistry of group 14 element compounds is a very active research area.[7] During the last decade, we have investigated the photochemical reactions of the radicals of heavy atoms such as Si, Ge, and Sn from the viewpoints of intermediates, kinetics, and excited states.[8-17] By means of laser flash photolysis and fluorescence lifetime measurements, we have found that the photolysis of some organosilicon and organogermanium compounds in cyclohexane gives group 14 element centered radicals.[8] In particular, we have found that the photodecomposition of aryl-substituted germanes occurs through the triplet excited states. The primary photochemical processes of these germanes (R_3GeAr)[8] are described in eqs 1-3. Thus, a triplet radical pair of germyl and aryl radicals

$$R_3GeAr \xrightarrow{h\nu} {}^1R_3GeAr^* \rightarrow {}^3R_3GeAr^* \tag{1}$$

$${}^3R_3GeAr^* \rightarrow {}^3\overline{R_3Ge^{\bullet}\,{}^{\bullet}Ar} \tag{2}$$

$${}^3\overline{R_3Ge^{\bullet}\,{}^{\bullet}Ar} \rightarrow R_3Ge^{\bullet} + Ar^{\bullet} \tag{3}$$

$$R = \text{aryl or alkyl, } Ar = \text{aryl}$$

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$(^3\overline{\mathrm{R_3Ge^\bullet\,{}^\bullet Ar}})$ is expected to be formed in the early stage of the photodecomposition of each germane. This reaction system seems to be favorable for the detection of magnetic field effects.

In the preliminary report,[18] we carried out a laser flash photolysis study of the photodecomposition of methyltriphenylgermane in a micellar solution at room temperature and found a magnetic field effect on the generated germyl radical. In the present paper, we report on a systematic study of the magnetic field effects on the photodecomposition of several silicon and germanium compounds in a micellar solution and in an oil emulsion. The correlation between the magnitudes of magnetic field effects and the reaction conditions is also discussed.

Experimental Section

Materials. Tetraphenylsilane (Ph_4Si (**1**), mp 232–233 °C),[19] tetraphenylgermane (Ph_4Ge (**2**), mp 226–228 °C),[20] methyltriphenylgermane (Ph_3MeGe (**3**), mp 69–71 °C),[21] and dimethyldiphenylgermane (Ph_2Me_2Ge (**4**), bp 144 °C/10 mmHg)[22] were prepared as described in the cited references. Xanthone was repeatedly recrystallized from ethanol.

Solvents. Water was deionized and distilled. Polyoxyethylene(23) dodecyl ether (Brij 35) was used as received. The concentration of Brij 35 in the employed micellar solution was 8.0×10^{-2} mol dm^{-3}. Hexadecylsulfuric acid sodium salt (SCS) was purified by repeated recrystallization from ethanol. Hexadecane and 1-pentanol were distilled. The oil emulsion was prepared by mixing SCS (2 g), 1-pentanol (4 mL) and hexadecane (1 mL), and water (24 mL). The micellar Brij 35 solutions and oil emulsions of **1**–**4** were made by sonication.

Photochemical Reaction. The irradiatioin of the sample was carried out with a 300-W Xe lamp (ILC Technology) and a 125-W low-pressure Hg arc lamp (Sen Tokushu Kogyou Co. Ltd.). The Xe lamp intensity was monitored by a photocell. Reaction products were analyzed by a gas chromatograph (GC), a GC–mass spectrometer, and a high-pressure liquid chromatograph (HPLC). GC–mass spectra were obtained with a JEOL JMS-DX 303 mass spectrometer. GC was performed on Simadzu GC-4CM and -8A instruments with 2-m 10% SE-30 and 2-m 10% OV-1 columns. HPLC was performed on a Waters Model 510 with a μBONDAPAC C18 column eluted by methanol–water (1/1). The product yield and disappearance rate were determined by comparison with authentic samples.

Laser Flash Photolysis. Laser flash photolysis experiments were performed on nitrogen-bubbled solutions at room temperature by using the fourth harmonic (266 nm) of a Quanta-Ray DCR-11 Nd:YAG laser as an exciting light source. The pulse width of the fourth harmonic was 5 ns. The laser flash photolysis apparatus was similar to that published elsewhere.[6a] In the present study, the time dependence of transient absorption intensities was recorded and analyzed by a combination of an Iwatsu DM901 transient recorder (10 ns/ch) and an NEC PC9801 microcomputer. Magnetic fields up to 1.35 T were provided by a Mitsubishi 6MA-EM1275A electromagnet. The strength of the magnetic field (B) was measured by an F. W. Bell Model 9200 gaussmeter. The lowest magnetic field generated by a counter current for canceling the residual field was less than 0.2 mT. Hereafter, the experiments under the lowest magnetic field are denoted as those in the absence of a magnetic field.

Results and Discussion

Time-Resolved Optical Absorption (TROA) Spectra. Since Ph_4Si (**1**) and Ph_4Ge (**2**) could not be dissolved in the Brij 35 micellar solution, the oil emulsion was used. On the other hand, Ph_3MeGe (**3**) and Ph_2Me_2Ge (**4**) were dissolved in the micellar solution. The concentrations of **1**–**4** in the employed Brij 35 micellar solution or oil emulsion were $1\text{–}1.5 \times 10^{-3}$ mol dm^{-3}. Laser flash photolysis was performed on solutions of **1**–**4** at room temperature. The time profile of the absorbance ($A(t)$) was measured in the wavelength region 300–600 nm upon irradiation with the fourth harmonic of the Nd:YAG laser. Using the $A(t)$ curves observed at different wavelengths in the absence of a magnetic field, the TROA spectra of **1**–**4** were obtained at the delay time of 200 ns after laser excitation. The typical results observed with **1** and **3** are shown in Figure 1. Similar spectra have also been obtained for **2** and **4**. Each of the spectra has a peak (λ_{max}) at 310–330 nm, and the obtained λ_{max} values are listed in Table I. Each observed spectrum can safely be assigned to the corresponding group 14 element centered radical generated by the homolysis of phenyl–E bond.

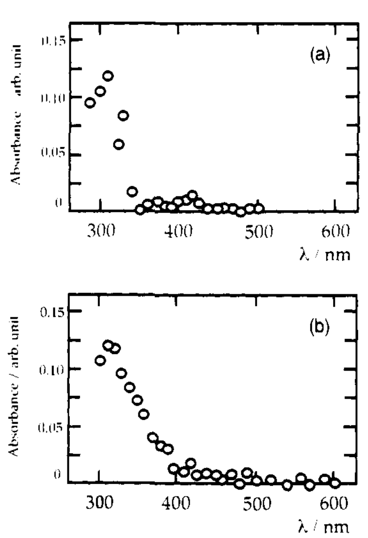

Figure 1. Transient absorption spectra observed at a delay time of 200 ns after laser excitation of (a) the oil emulsion of Ph_4Si (**1**) and (b) the Brij 35 micellar solution of Ph_3MeGe (**3**) at room temperature.

Table I. Transient Absorption Spectral Data for Aryl-Substituted Group 14 Compounds

compd	assignment	λ_{max} (nm)	ref
Ph_4Si (**1**)	$Ph_3Si^\bullet$	315	this work
Ph_3SiLi^a	$Ph_3Si^\bullet$	320	9
Ph_4Ge (**2**)	$Ph_3Ge^\bullet$	310	this work
Ph_3GeLi^a	$Ph_3Ge^\bullet$	330	9
$Ph_3GeCOPh^b$	$Ph_3Ge^\bullet$	325	13
Ph_3MeGe (**3**)	$Ph_2MeGe^\bullet$	320	this work
$Ph_2MeGeLi^a$	$Ph_2MeGe^\bullet$	330	9
Ph_2Me_2Ge (**4**)	$PhMe_2Ge^\bullet$	320	this work
$PhMe_2GeLi^a$	$PhMe_2Ge^\bullet$	315	9
$PhMe_2GeCOPh^b$	$PhMe_2Ge^\bullet$	315	13

[a] In THF. [b] In cyclohexane.

$$\mathrm{Ph}_n\mathrm{Me}_{4-n}\mathrm{E} \xrightarrow{h\nu} \mathrm{Ph}_{n-1}\mathrm{Me}_{4-n}\mathrm{E}^\bullet + {}^\bullet\mathrm{Ph} \qquad (4)$$

$$\mathrm{E} = \mathrm{Si\ and\ Ge},\ n = 2\text{–}4$$

This assignment can be derived from the following reasons: (1) The spectral shapes and peak positions observed for **1**–**4** agree with those of the corresponding radicals ($Ph_{n-1}Me_{4-n}E^\bullet$) reported previously.[8-17] (2) Upon irradiation of the oil emulsion containing **1** and the Brij 35 micellar solution containing **3** with a 125-W low-pressure Hg arc lamp for 6 h in the presence of carbon tetrachloride, triphenylchlorosilane (Ph_3SiCl) and methyldiphenylchlorogermane ($Ph_2MeGeCl$) were obtained in high yields, respectively. Carbon tetrachloride is a well-know trapping reagent for silyl and germyl radicals.[23] Thus, Ph_3SiCl and $Ph_2MeGeCl$ should be produced from $Ph_3Si^\bullet$ and $Ph_2MeGe^\bullet$ through the following reaction.

$$\mathrm{Ph}_{n-1}\mathrm{Me}_{4-n}\mathrm{E}^\bullet + \mathrm{CCl_4} \rightarrow \mathrm{Ph}_{n-1}\mathrm{Me}_{4-n}\mathrm{ECl} + {}^\bullet\mathrm{CCl_3} \qquad (5)$$

It is noteworthy that the main product was not Ph_3GeCl but $Ph_2MeGeCl$ for **3**. This fact shows that the bond fission of Ph–Ge occurs mainly as shown in eq 4.

No transient absorption band due to the phenyl radical was observed. The wavelength of its absorption peak and its molar extinction coefficient were reported to be 260 nm and 630 mol^{-1} dm^{-3}, respectively.[24] Thus, the phenyl radical should have no

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Table II. Magnetic Field Dependence of the Decay Rate Constant of the Fast Component Observed at 320 nm

	k_f, 10^6 s^{-1} ^{a}						
	Ph_4Si (**1**)	Ph_4Ge (**2**)	Ph_3MeGe (**3**)			Ph_2Me_2Ge (**4**)	
magnetic field, T	D_{emu}^{b}	D_{emu}^{b}	D_{emu}^{b}	D^b	T^b	D^b	$T^{b,c}$
0.0	1.39	0.79	0.9	1.07	0.73	1.01	0.94
0.05				0.99			
0.10				0.88			
0.30				0.87			
0.50				0.82			
0.75				0.78			
1.00	0.72	0.53	0.72	0.75	0.53	1.02	0.59
1.35	0.88		0.67	0.73		1.02	

[a] The experimental errors of k_f are within ±0.03 × 10^6 s^{-1}. [b] D, D_{emu}, and T mean direct excitation in Brij 35, direct excitation in oil emulsion, and triplet sensitization with xanthone in Brij 35, respectively. [c] Observed at 340 nm.

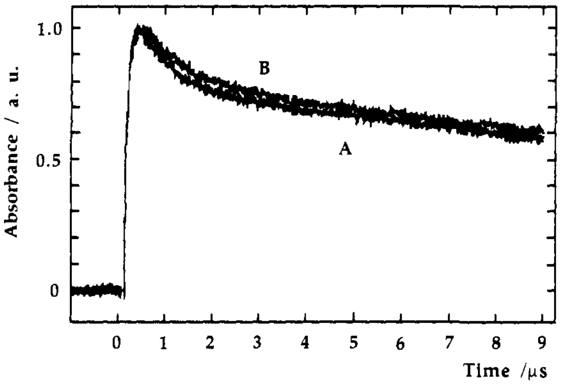

Figure 2. $A(t)$ curves at 320 nm observed by direct excitation of Ph_4Si (**1**) in the oil emulsion (A) in the absence and (B) in the presence of a magnetic field of 1.35 T.

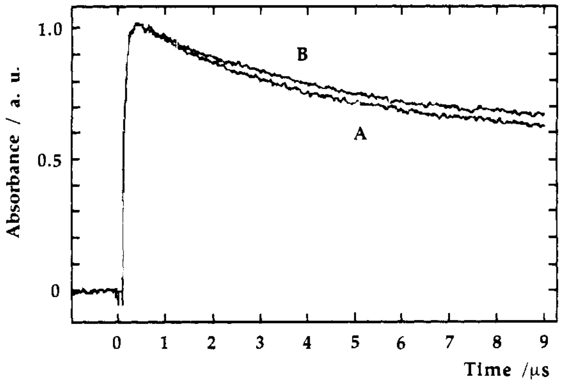

Figure 3. $A(t)$ curves at 320 nm observed by direct excitation of Ph_4Ge (**2**) in the oil emulsion (A) in the absence and (B) in the presence of a magnetic field of 1.0 T.

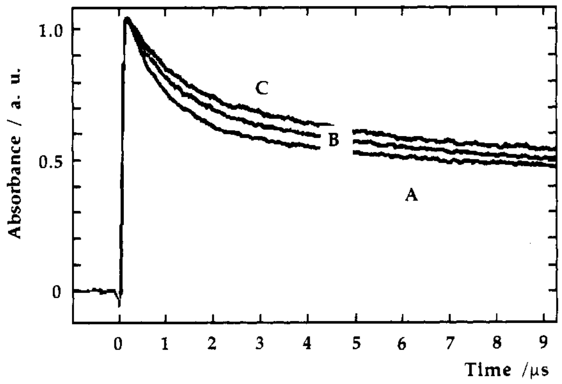

Figure 4. $A(t)$ curves at 320 nm observed by direct excitation of Ph_3MeGe (**3**) in the micellar Brij 35 solution in the absence (A) and in the presence of magnetic fields of 0.5 T (B) and 1.35 T (C).

Table III. Magnetic Field Dependence of the Decay Rate Constant of the Slow Component Observed in the Presence and Absence of Magnetic Fields below 1.35 T

compd	k_s s^{-1} (0 T ≤ B ≤ 1.35 T)
Ph_4Si (**1**)^a	(4.8 ± 0.7) × 10^4
Ph_4Ge (**2**)^a	(3.1 ± 0.5) × 10^4
Ph_3MeGe (**3**)^b	(2.5 ± 0.3) × 10^4
Ph_2Me_2Ge (**4**)^b	(2.3 ± 0.5) × 10^4

[a] Observed at 320 nm in oil emulsion. [b] Observed at 320 nm in Brij 35.

absorption in the observed wavelength region (300–600 nm) of Figure 1. It is possible that the phenyl radical is reacting with a Brij 35 or a SCS molecule (R′H) which forms the Brij 35 micelle or the oil emulsion, respectively.

$$Ph^\bullet + R'H \rightarrow PhH + {}^\bullet R' \qquad (6)$$

If this hydrogen abstraction occurs, benzene should be produced as a main product. The yield of benzene was examined by HPLC. Upon photolysis of **3** in the Brij 35 micellar solution and in the oil emulsion at room temperature with the low-pressure Hg lamp for 10 min, the yield of benzene was obtained to be 15.7% and 16.4% of the total decomposition of Ph_3MeGe, respectively. This result indicates that reaction 6 is a minor path in the present study.

In these systems, the fluorescence lifetimes of **1–4** were found to be shorter than the time resolution of the present apparatus (10 ns). The transient absorption bands which might be assigned to the triplet–triplet absorptions of **1–3**, respectively, were also found in the wavelength region 450–550 nm, and those decay times were ca. 50 ns. As shown in Figures 2–4, each of the peaks at 310–320 nm obtained for **1–3** grew with a rise time of ca. 50 ns. From these results, we can conclude that the photodecomposition of **1–3** occurs through their triplet excited state. Thus, these reactions can be reprsented by the reactions shown in Scheme I. On the other hand, the photodecomposition of **4** occurs mainly through the singlet state as described later.

Magnetic Field Dependence of *A* (*t*) Curves. The time profiles of the absorbance ($A(t)$) in the wavelength region 310–330 nm were measured in the presence of magnetic fields of 0–1.35 T. Some typical results are shown in Figures 2–4. We can see from these results that the $A(t)$ curves obtained for **1–3** are appreciably changed by the field strength. The $A(t)$ curves have fast and slow decay components. In comparison with the results obtained for some ketones in micelles,[6] the fast component can safely be ascribed to the corresponding silyl and germyl radicals inside radical pairs and the slow one to the escaped radicals. From each of the occupation numbers of **1–4** in a Brij 35 micellar solution (<0.75) for an oil emulsion (<0.5), at most one radical pair should be formed in a single micelle or emulsion. The slow decay of the escaped radical is probably due to the quenching by oxygen left after nitrogen bubbling and/or by water in the Brij 35 micellar solution or the oil emulsion. Thus, we have analyzed the decay profiles of the $A(t)$ curves by the nonlinear least-squares method for the following equation:

$$A(t) = I_f \exp(-k_f t) + I_s \exp(-k_s t) \qquad (7)$$

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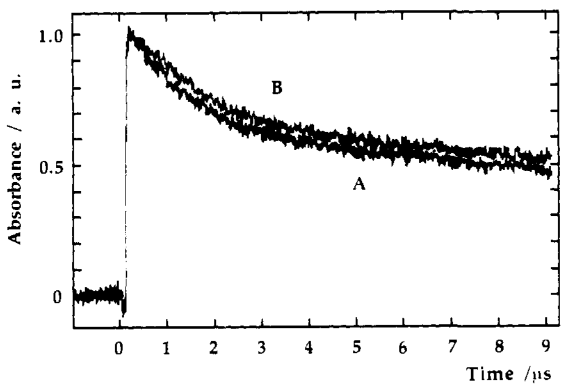
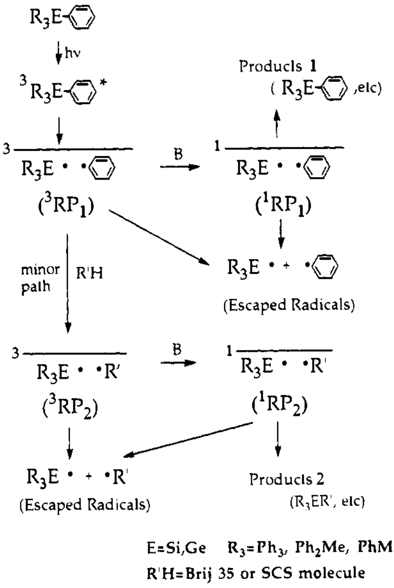


Figure 5. $A(t)$ curves at 340 nm observed by triplet sensitization of Ph_2Me_2Ge (**4**) in the micellar Brij 35 solution (A) in the absence and (B) in the presence of a magnetic field of 1.0 T.

Scheme I



Here, $A(t)$ is the absorption intensity at a delay time of t after the laser excitation ($t = 0$), k_f and k_s are the fast and slow decay rate constants, respectively, and I_f and I_s represent the corresponding pre-exponential factors. From the analysis of the observed $A(t)$ curves by eq 7, the k_f and k_s values were determined as listed in Tables II and III, respectively.

The obtained k_s values did not show any appreciable magnetic field effect beyond the experimental error as shown in Table III. This fact means that the quenching reaction of the escaped silyl and germyl radicals is independent of magnetic fields below 1.35 T. In contrast to the k_s values, the k_f values obtained for **1**–**3** decreased with increasing B from 0 to 1.35 T as shown in Table II. For example, the k_f value of **3** was obtained to be $(1.07 \pm 0.03) \times 10^6\ s^{-1}$ at 0 T and decreased to $(0.73 \pm 0.03) \times 10^6\ s^{-1}$ at 1.35 T. This is the first direct observation of a magnetic field effect on the dynamic behavior of a radical involving a heavier atom than S as a radical center. Table II shows that the lifetimes of the triplet radical pairs consisting of the group 14 element centered and C-centered radicals are substantially (up to 47% for direct excitation of **3**) increased by magnetic fields below 1.35 T for **1**–**3**.

On the other hand, no magnetic field effect was observed for the k_f value obtained upon direct excitation of **4** in the Brij 35 micellar solution. This fact indicates that the photodecomposition of **4** by direct excitation mainly occurs through its singlet state. Thus, we investigated the magnetic field effect on the photodecomposition of **4** by triplet sensitization in the Brij 35 micellar solution. For comparison, the laser flash photolysis by triplet sensitization was also carried out for **3** in the micellar solution. Xanthone was used as a triplet sensitizer. We measured the $A(t)$ curve at 340 nm. Figure 5 shows the $A(t)$ curves observed with **4** in the absence and presence of a magnetic field of 1.0 T. We can see from this figure that the $A(t)$ curve is appreciably changed by the field. The decay profiles of the $A(t)$ curves were also analyzed by eq 7. The obtained k_f value at 1.0 T ($0.59 \times 10^6\ s^{-1}$) was found to be smaller than the value at 0 T ($0.94 \times 10^6\ s^{-1}$) as shown in Table II. A similar result was also obtained for the triplet sensitization of **3** as listed in Table II. Thus, the magnetic field effects obtained for the triplet sensitization of **3** and **4** were found to be very similar to those obtained for the direct excitation of **1**–**3**. The lack of the magnetic field effect on the direct excitation of **4** seems to be due to direct decomposition through its singlet excited state.

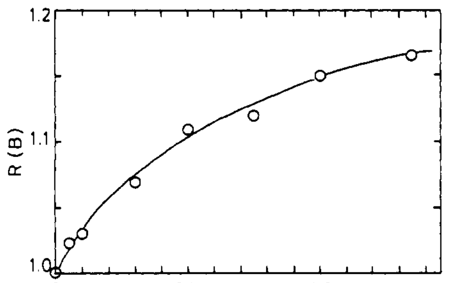


Figure 6. Magnetic field dependence of the ratio $R(B) = Y(B)/Y(0)$ at 330 nm observed by direct excitation of Ph_3MeGe (**3**) in the micellar Brij 35 solution. The experimental errors of $R(B)$ is within ±0.02.

Table IV. The Ratio of the Relative Yield of the Escaped Group 14 Centered Radical at 1.0 T versus the Yield at 0 T

compd	soln[a]	$R(1.0T)$[d]
Ph_4Si (**1**)	emulsion (D)[b]	1.08
Ph_4Ge (**2**)	emulsion (D)[b]	1.05
Ph_3MeGe (**3**)	emulsion (D)[b]	1.18
	Brij 35 (D)[b]	1.15
	(T)[b]	1.21
Ph_2Me_2Ge (**4**)	Brij 35 (D)[b]	1.0
	(T)[c]	1.11

[a] D and T mean direct excitation and triplet sensitization with xanthone, respectively. [b] Observed at 320 nm. [c] Observed at 340 nm. [d] The experimental errors of $R(B)$ are within ±0.02.

Table II shows that the k_f values obtained at 0 T for the present studies are about $10^6\ s^{-1}$. These values are much smaller than those expected from the triplet–singlet (T–S) conversion of the radical pairs through the hyperfine coupling mechanism (HFCM).[1-3] The rate-determining step of the fast decay, however, should be the coupling reaction of the singlet radical pairs.[25]

Because the lifetimes of the triplet radical pairs listed in Table II are shorter than 2 µs, we can safely assume that the $A(4\mu s)$ values obtained for **1**–**4** are almost all due to the escaped silyl and germyl radicals. That is, the $A(4\ \mu s)/A(0\ \mu s)$ ($=Y$) ratio can represent the relative yields of the escaped radicals. Thus, we can see that the $Y(B)/Y(0)$ ratio ($=R(B)$) observed in the presence of a magnetic field gives the magnetic field effect on the yield of each escaped silyl or germyl radical. The plots of $R(B)$ for **3** against B are shown in Figure 6. This curve shows that $R(B)$ increased with increasing B and that $R(1.35\ T)$ reached 1.16 ± 0.02. Similar results were obtained for **1**–**4**, except for the direct excitation of **4**. The obtained $R(1.0\ T)$ values are summarized in Table IV. The yields of the escaped silyl and germyl radicals generated from the triplet radical pairs increase with increasing B. Thus, it seems that the obtained magnetic field effects on $R(B)$ and k_f are explained by the same mechanism.

Mechanisms of Reactions and Magnetic Field Effects. In order to confirm the reaction process shown in Scheme I, we tried to measure the magnetic field effect on the disappearance rate of **3**. In Scheme I, Products 1 come from the radical pair of $R_3E^•$

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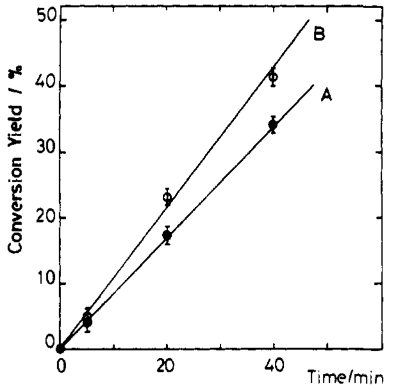


Figure 7. Magnetic field dependence of the conversion yields of Ph_3MeGe (3) in the micellar Brij 35 solution obtained (A) in the absence and (B) in the presence of a magnetic field of 1.0 T. The experimental errors of the conversion yield is within ±1.5%.

and •Ph (RP_1) and Products 2 from the pair of $R_3E^•$ and •R′ (RP_2). The main product among Products 1 is the starting compound (3). If RP_1 is dominant in this reaction, the disappearance rate of 3 should also increase with increasing B, because the yield of the escaped radical ($R_3E^•$) was found to be increased by the magnetic fields. On the other hand, if RP_2 is dominant in this reaction, the yield of Products 2 should decrease with increasing B, and the disappearance rate of 3 should not be affected by the fields. Thus, the conversion yield of 3 was investigated in the absence and presence of a magnetic field of 1.0 T using the Xe lamp. The plots of the conversion yield observed with 3 in the Brij 35 micellar solution against irradiation time are shown in Figure 7. The concentration of 3 before irradiation was 6.6 × 10^{-3} mol dm^{-3}. Using the slopes of Figure 7 and the starting concentration of 3, the disappearance rates were obtained to be (3.6 ± 0.2) × 10^{-3} mol dm^{-3} h^{-1} at 0 T and (4.3 ± 0.2) × 10^{-3} mol dm^{-3} h^{-1} at 1.0 T. The fluctuation of the Xe lamp intensity was less than 1%. From this fact, it has been concluded that RP_1 is dominant in this reaction.

The obtained magnetic field effects of k_f and $R(B)$ can be interpreted in terms of a combination of the hyperfine coupling and the relaxation mechanisms (HFCM and RM)[6a,25] for the triplet precursors. In each generated triplet radical pair, T–S mixing occurs for all triplet levels through the HFCM in the absence of a magnetic field. Because the triplet levels split into three sublevels (T_0, T_{+1}, and T_{-1}) in the presence of a magnetic field, the $T_{\pm1}$–S mixing is almost forbidden after application of the field. The magnetic field effect due to the HFCM, however, should be saturated at a relatively low field. The half-field ($B_{1/2}$) of the saturation is given as follows:[26]

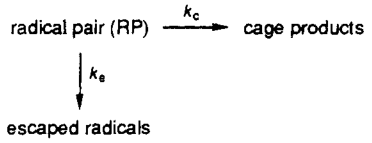
$$B_{1/2} = 2(B_1^2 + B_2^2)/(B_1 + B_2) \tag{8}$$

The individual B_i value characterizing the radical (i = 1 or 2) is given by

$$B_i = (\sum_j I_{ij}(I_{ij} + 1)a_{ij}^2)^{1/2} \tag{9}$$

Here, a_{ij} is the isotropic HFC constant of the jth nuclear in radical i. Among the stable isotopes of Ge, ^{73}Ge is only the magnetic one and its natural abundance is 7.8%. The other stable isotopes (92.2%) are nonmagnetic. For such nonmagnetic Ge isotopes, the $B_{1/2}$ value is calculated to be 1.4 mT for RP_1 of 3. Thus, magnetically induced changes of RP_1 without ^{73}Ge should be saturated below 0.1 T when the HFCM is dominant. On the other hand, the changes due to the RM should last at higher fields. According to the RM, the relaxations from T_{+1} and T_{-1} to T_0 and S are taken into consideration. The relaxation rate should decrease with increasing B.[25] The magnetic field effects observed for k_f and $R(B)$ at high fields (B > 0.1 T) can be explained by the RM.

Scheme II



The decrease of k_f by the HFCM and RM reduces the recombination rate of the radical pair and enhances the yield of the escaped radicals. Thus, the magnetically induced increases obtained in the present study for the lifetimes of the triplet radical pairs and the yields of the escaped silyl and germyl radicals can be interpreted by the HFCM and RM.

Magnitude of Observed Magnetic Field Effects. From a simple kinetic model, the competition between the cage recombination of a radical pair and the escape from the pair can be represented by Scheme II. Here, k_c is the rate constant of the cage recombination inside a radical pair and k_e is that of the escape from the pair. Thus, the yield of the escaped radical (Y) can be described as follows:

$$Y = k_e/(k_c + k_e) \tag{10}$$

Because $k_c + k_e$ can be represented by the experimentally obtained k_f value, the $R(B)$ value is expressed as follows:

$$R(B) = \frac{Y(B)}{Y(0)} = \frac{k_f(0)}{k_f(B)} \tag{11}$$

As shown in Tables II and IV, the $R(B)$ values are somewhat smaller than the corresponding $k_f(0)/k_f(B)$ values. This discrepancy can be explained by a more quantitative analysis with the Stochastic Liouville equation, but this is the beyond the scope of the present study.

The magnitudes of the observed magnetic field effects in the present study are much smaller than those observed previously in the reactions of ketones in micellar solutions at room temperature.[6] In the present study, each of the produced radical pairs consists of Si- and Ge-centered and C-centered radicals. On the other hand, the radical pairs in the previous reports consisted of only C-centered radicals. The largest R(1.0 T) value in the present study is 1.21 ± 0.02, as shown in Table IV, while the R(1.0 T) values in the previous studies often exceeded 5. This difference is ascribed to the existence of silyl or germyl radicals in each radical pair in the present study. Previously, the R(1.0 T) value was obtained to be as small as 1.27 for the yield of the escaped ketyl radical which was generated from the hydrogen abstraction reaction of triplet xanthone with triethylgermane in an SDS (sodium dodecyl sulfate) micellar solution.[5] Here, the generated radical pair consisted of the germyl and ketyl radicals. The SO interaction of a heavy atom such as Si and Ge seems to enhance the relaxation of the T_{+1} and T_{-1} sublevels. Therefore, the relaxation rates of T_{+1} and T_{-1} of the radical pairs generated in the present study should become much faster than the rates of the pairs consisting only C-centered radicals.

There are differences in the magnetic field effects observed for the reactions of the Si- and Ge-centered radicals. Table II shows that the k_f(0 T)/k_f(1.0 T) value obtained for **1** is 1.93, and that obtained for **2** is 1.49. Table IV shows that the R(1.0 T) value obtained for **1** is 1.08, and that obtained for **2** is 1.05. Thus, the magnetically induced changes of **1** are slightly larger than those of **2**. This difference can be explained by the fact that the relaxation rates of the T_{+1} and T_{-1} sublevels of **2** should be faster than those of **1**, because of the larger SO interaction of Ge than of Si.

As shown in Table IV, the R(1.0 T) values of **2**–**4** increase in the following order:

$$R(1.0\ \mathrm{T})\ \text{for}\ \mathbf{2} \approx R(1.0\ \mathrm{T})\ \text{for}\ \mathbf{4} < R(1.0\ \mathrm{T})\ \text{for}\ \mathbf{3} \tag{12}$$

This substituent effect may be explained by a combination of the SO interaction and the steric environments around the germanium atom. The spin densities of Ge (ρ_{Ge}) of the generated germyl radicals were reported[27] to be in the following order:

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(26) Weller, A.; Nolting, F.; Staerk, H. *Chem. Phys. Lett.* **1983**, *96*, 24.

$$\rho_{Ge}(Ph_3Ge^\bullet) \text{ for } \mathbf{2} = 0.82 < \rho_{Ge}(Ph_2MeGe^\bullet) \text{ for } \mathbf{3} = 0.86 < \rho_{Ge}(PhMe_2Ge^\bullet) \text{ for } \mathbf{4} = 0.91 \quad (13)$$

From the effect of the SO interaction of Ge, the larger ρ_{Ge} is the faster the relaxation rate becomes. Thus, the order of $R(B)$ should become as follows:

$$R(1.0\ T) \text{ for } \mathbf{4} < R(1.0\ T) \text{ for } \mathbf{3} < R(1.0\ T) \text{ for } \mathbf{2} \quad (14)$$

The order of relation 14 differs from that of relation 12. This discrepancy can be explained by the hindered environment of $Ph_3Ge^\bullet$: the steric hindrance of $Ph_3Ge^\bullet$ reduces the recombination rate of its radical pair, resulting in the relaxation of the T_{+1} and T_{-1} sublevels before the recombination. Thus, the $R(1.0\ T)$ value of **2** would be reduced to the value of **4**.

As shown in Tables II and IV, there is no large difference in the magnetically induced changes between the $R(B)$ values observed in the Brij 35 micellar solution and the oil emulsion. This fact could be due to the size effect on the decay of triplet-derived radical pairs.[28] The size of the Brij 35 micelle can be estimated to be 50–100 Å.[29] The oil emulsion of the present system (SCS–pentanol–hexadecane–water) has a micellelike aggregate of a similar dimension (typically ~100 Å).[32] Since there is no difference between the size of the Brij 35 micelle and that of the oil emulsion, the k_c and k_e values in the Brij 35 micelle are expected to be similar to those in the oil emulsion. Thus, it is reasonable that similar magnetically induced changes were obtained for both solutions. On the other hand, the size of normal ionic micelles such as SDS micelle are estimated to be 10–20 Å.[33] In such smaller micelles, the k_c and k_e values would be expected to be larger than those in the Brij 35 micelle and oil emulsion.[28] If k_c becomes much larger than the relaxation rates of the T_{+1} and T_{-1} sublevels, it is probable that the magnetically induced changes in such smaller micelles would be observed to be larger than those in the Brij 35 and the oil emulsion. Unfortunately, the present materials (**1–4**) are not soluble in such ionic micellar systems.

In order to observe large magnetic field effects on the radical reactions of compounds containing heavy atoms such as Si, S, Ge, and Sn, the compounds must be designed to meet the following criteria. (1) Starting compounds should be dissolved in normal ionic micelles such as SDS. (2) Reactions should occur through triplet precursors. (3) Generated radical pairs should have moderate reactivity. (4) To weaken the SO interaction, spin density on a heavy atom should be small.

Thus, the magnitude of the magnetic field effects of heteroorganic radicals containing heavy atoms is inclined to decrease from that of organic radicals through the spin–orbit interactions of heavy atoms. However, it is noteworthy that the radical pairs involving silyl and germyl radicals still gave some magnetic field effects in the present reactions. Therefore, it seems hopeful to separate ^{29}Si and ^{73}Ge with this kind of reaction through the magnetic isotope effect.

Conclusion

In the present laser flash photolysis studies of aryl-substituted silicon and germanium compounds in micellar Brij 35 solutions and oil emulsions, we have found that the lifetimes of the triplet radical pairs and the yields of the escaped radicals increased with increasing B. In the largest case, the yield of the escaped germyl radical and the lifetime of the triplet radical pair at 1.0 T increased by 21% and 92%, respectively, in comparison with those at 0 T. These magnetic field effects can be interpreted in terms of the HFCM and the RM.

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(29) For polyoxyethylene alkyl ethers ($C_{16}H_{33}(OCH_2CH_2)_nOH$, $n = 18$, 30), their aggregation numbers (N_{ag}) and molecular weights (MW) are 50 and 1034 (for $n = 18$) and 30 and 1442 (for $n = 30$), respectively.[30] The total micellar molecular weights ($=N_{ag}$MW) of these micelles are calculated to be 51 700 (for $n = 18$) and 43 260 (for $n = 30$). The sizes of these micelles were reported to be 69 (for $n = 18$) and 72 Å (for $n = 30$).[31] On the other hand, the total micellar molecular weight of Brij 35, 47 920 ($N_{ag} = 40$, MW = 1198), is similar to those of the above micelles. Therefore, the micellar size of Brij 35 is estimated to be 50–100 Å.

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